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ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSES: ASSISTANCE PROJECTS, FY75

by

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Project No. 16020 GHZ

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure chemical pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of specific environmental contaminants, the Analytical Chemistry Branch develops techniques for identifying and measuring chemical pollutants in water and soil.

This report is the fifth in a series of annual summaries of analytical chemistry support requested by other organizations. In most cases, these analyses contributed to the solution or better understanding of a pollution incident. This report will acquaint other researchers and administrators with the type of information that can be obtained with current analytical techniques.

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ABSTRACT

The Analytical Chemistry Branch of the Athens Environmental Research Laboratory identified and measured aquatic pollutants under eight projects in response to requests for assistance from other EPA organizations and other government agencies. In most cases these analyses helped us to solve, or at least to understand more clearly, the related pollution incident, and in some cases the analyses provided evidence for enforcement of regulatory legislation. Under an additional project, analytical consultations were held as requested by various organizations concerned with pollution incidents. The report describes those projects.

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LIST OF ABBREVIATIONS

AAS	-	atomic absorption spectrophotometry
ACB	-	Analytical Chemistry Branch
EPA	-	U.S. Environmental Protection Agency
GC	-	gas chromatography
GC-FTIR	-	combined gas chromatography and Fourier transform infrared spectrophotometry
GC-MS	-	combined gas chromatography and mass spectrometry
INAA	-	instrumental neutron activation analysis
LMRF	-	Lower Mississippi River Facility
MS	-	mass spectrometry
NFIC	-	National Field Investigations Center of the Environmental Protection Agency
NOAA	-	National Oceanic and Atmospheric Administration
PCB	-	polychlorinated biphenyl
SSMS	-	spark source mass spectrometry

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SECTION I

INTRODUCTION

The Analytical Chemistry Branch (ACB) at the Athens Environmental Research Laboratory (Athens ERL) develops techniques for identifying and quantifying chemical pollutants and identifies specific compounds associated with various pollution sources. The ACB has analyzed many samples related to a variety of specific pollution problems. Analytical results were reported only to the persons who requested the analyses and therefore had limited distribution. Earlier problems studied by the ACB have been summarized in annual reports[1-4] to acquaint other researchers and administrators with the type of information that can be obtained and to inform environmental chemists of technique applications and developments. This report summarizes fiscal year 1975 projects.

SECTION II

RECOMMENDATIONS

Existing analytical techniques should be continually improved, and new techniques should be investigated for applicability to pollutant analysis. Information about specific pollution incidents should be widely disseminated to help solve and perhaps prevent future environmental problems.

SECTION III

DISCUSSION

CHEMICAL ELEMENTS IN GREAT LAKES FISH SAMPLES

To provide baseline data for future pollution studies, Environment Canada, through the U.S. Bureau of Sport Fisheries and Wildlife in Ann Arbor, Michigan, requested spark source mass spectrometric (SSMS) survey analyses of chemical elements in four fish samples. Personnel from Environment Canada collected samples of chubs and burbot from Lake Huron and lake trout from Coppermine Point and Apostle Island in Lake Superior. Each sample was an entire fish carcass, including intestines, that was ground, blended, frozen, and shipped to the Athens Environmental Research Laboratory, where it was prepared for SSMS analysis.

After addition of yttrium as an internal standard, a 5-g aliquot of each sample was digested in 50 ml of formic acid for 6 hr to destroy proteinaceous material. Graphite was added, and each sample was dried under infrared light. To destroy all remaining organic material, each sample was heated in a muffle furnace at 460°C for 6 hr.

Duplicate analyses of the four fish samples provided concentration data for 38 elements (Table 1). Four other elements (Zr, Cu, Ni, and Al) that were detected in the fish samples were not reported, because comparable amounts were found in the blank sample. These elements were probably introduced during formic acid digestion.

These data were reported to the supervisory chemist of the Analytical Chemistry Group of Environment Canada in Winnipeg, Manitoba, where they will be compiled with other pollution parameters and maintained for future use.

Table 1. CHEMICAL ELEMENTS DETECTED BY SSMS IN GREAT LAKES FISH SAMPLES

Element	Concentration, µg/kg[a]			
	Lake Superior Samples		Lake Huron Samples	
	Trout from Coppermine Point	Trout from Apostle Island	Burbot	Chubs
Ca	>45,000	>71,000	>54,000	>27,000
P	>26,000	>38,000	>26,000	>15,000
Na	>24,000	>32,000	>25,000	>14,000
S	>23,000	>22,000	>22,000	>60,000
Zn	21,000	27,000	76,000	25,000
I	16,000	25,000	16,000	12,000
K	>16,000	>16,000	>13,000	> 6,000
Fe	14,000	12,000	22,000	11,000
Mg	7,000	82,000	22,000	9,000
Sn	7,000	430	820	350
Cl	> 5,000	>53,000	>50,000	>60,000
Br	3,100	8,200	8,500	5,300
Rb	2,800	3,800	2,400	2,200
Mn	2,700	3,700	1,700	2,400
Cr	1,600	980	680	1,800
Sr	1,200	2,200	3,200	3,800
Co	360	370	240	1,000
Ce	240	270	160	1,300
Se	180	200	190	280
Ti	160	200	130	160
Pb	100	110	95	75
V	85	85	75	260
Ba	55	120	250	300
Sc	55	120	75	440
Ag	45	180	60	80
In	30	130	25	55
Mo	25	220	30	N.D.
F	20	460	830	270
Ga	15	5	20	120
Cs	10	20	N.D.	N.D.
As	2	5	5	13
La	N.D.	130	25	60
Te	N.D.	10	50	N.D.
Cd	N.D.	N.D.	N.D.	170
Nd	N.D.	35	N.D.	N.D.
Rh	N.D.	20	N.D.	N.D.
Pr	N.D.	N.D.	N.D.	20
Ce	N.D.	5	N.D.	N.D.

a Average of duplicate analyses.

b Not detected; detection level is 0.5 µg/kg.

MULTIELEMENT ANALYSIS OF POULTRY FARM WATER SAMPLES

Investigation of possible causes of a poultry liver disease prompted a request for the ACB to analyze chemical elements in farm water samples. The incidence of this disease, Fatty Liver Syndrome (FLS), was much greater among laying hens in south Georgia than in north Georgia. The disease was suspected to be related to the presence of manganese in the hens' drinking water, because manganese had been correlated with fat accumulation in rats.

Scientists in the Department of Poultry Science at the University of Georgia were studying the problem under the auspices of the Georgia Egg Commission and requested the ACB's assistance. Instrumental neutron activation analysis of water samples was desired to confirm manganese concentration data that had been obtained by emission spectrography and to provide information about other chemical elements present.

The ACB was given samples that had been collected from 9 farms with a history of FLS and from 14 farms without any apparent FLS problem. Each 1-liter sample had been collected in a plastic bottle at the point where the chickens received drinking water. After a preservative (chloroform) was added, the samples were transported to the University and divided into aliquots for analysis.

Several elements (Mn, Ca, Mg, Sn, Na, Fe, Cu, Zn, Al, and B) were detected and measured with a direct reading emission spectrograph at the Soil Testing Laboratory of the University Cooperative Extension Service. Instrumental neutron activation analysis (INAA) by ACB personnel provided manganese concentration data and detected other chemical elements present at concentrations ≤ 1 µg/l, the approximate detection level for most elements.

No correlation between manganese content and geographic location of the sampling sites was revealed by INAA data. Manganese content varied from a level that could not be detected to 65 µg/l, with mean values of 8.5 $\pm$2.1 µg/l in water samples from farms without the disease and 19.6 $\pm$8.0 µg/l from those with the disease. These INAA manganese concentration data correlated with the emission spectrographic analyses, which produced mean values of 7.0 $\pm$2 µg/l and 14.7 $\pm$7 µg/l, respectively.

The INAA manganese concentration data and a list of all elements detected were reported to the scientists at the University's Department of Poultry Science. Their comparison of INAA data with emission spectrographic data produced a possible

correlation between the Fatty Liver Syndrome and water hardness. Most poultry farms with the disease problem had water with considerably higher concentrations of calcium and magnesium than were found in water samples from farms without the disease. The University of Georgia scientists concluded that further investigation is necessary to determine whether lipid metabolism in laying hens is directly related to the mineral content of their drinking water.

CHEMICAL ELEMENTS IN DRINKING WATER SAMPLES

To compare and evaluate several methods for multielement analysis of chemical elements in water, the EPA's Health Effects Research Laboratory in Cincinnati, Ohio, requested multielement analysis of about 100 drinking water samples. The ACB agreed to analyze all of these samples with neutron activation and to obtain comparative data for about 10 of these samples by analyzing them with SSMS.

Drinking water samples collected from all over the country were used for these comparative analyses. The first 39 samples requiring neutron activation analysis arrived at the Athens ERL in April and May 1975 and some analyses were completed in the latter part of FY 75. Preliminary INAA data indicated that Public Health Service water quality criteria for copper, manganese, cadmium, and chromium might have been exceeded at one or more sampling sites. Three samples requiring SSMS analysis arrived in May 1975, and quantitative data for 40 elements were obtained from duplicate analyses.

Work on this project will continue during FY 76. As data are obtained, they are reported to the Health Effects Research Laboratory, where they will be correlated with data from other analytical methods.

MERCURY IN SEAWATER

To confirm unexpectedly high mercury concentrations in seawater samples analyzed by atomic absorption spectrophotometry (AAS), the EPA's Region II Quality Control Coordinator requested neutron activation analysis of four seawater samples. These samples had been collected about 150 miles offshore of New Jersey at the 106 mile ocean dump site, the deepest and farthest offshore site assigned to industries with permits for ocean dumping. This site is intended for the most toxic and hazardous wastes and is monitored periodically by the National Oceanic and

Atmospheric Administration (NOAA) to guard against environmental degradation.

In the summer of 1974, samples collected at this site by NOAA were analyzed by AAS at the EPA Region II laboratory. Levels of mercury were 20 times higher than previously encountered concentrations. To confirm the AAS data, four of these samples were sent to the ACB for analysis by another technique. Mercury concentration data obtained from duplicate neutron activation analyses (Table 2) confirmed those obtained with AAS. Because sample contamination during collection procedures was thought to be the probable cause of these high mercury concentrations, the Quality Control Coordinator recommended that no action be taken unless Region II AAS analysis of the next set of samples, collected with careful attention to possible contamination sources, indicated that they also contained high levels of mercury.

Table 2. MERCURY IN SEAWATER SAMPLES ANALYZED BY NEUTRON ACTIVATION

Sample #	Mercury Concentration, µg/kg		
	Run 1	Run 2	Average
1	2.65	2.57	2.61
2	3.94	3.41	3.68
3	2.84	3.09	2.96
4	11.7	13.9	12.8

CHEMICAL ELEMENTS IN PLANT AND SOIL SAMPLES FOR BIOMONITORING OF POWER PLANT EMISSIONS

To determine if certain desert plants can be used for biological monitoring of chemical elements emitted from power plant smokestacks, the EPA's Environmental Monitoring and Support Laboratory (EMSL) at Las Vegas, Nevada, requested multielement analyses of plant tissues and soil samples. They hoped to correlate sampler chemical element content with stack gas

composition and with distance of the sampling site from the power plant.

Initially, neutron activation analysis of five standard samples was requested to confirm mercury and cadmium concentration data obtained by Zeeman spectroscopy, a new instrumental method in use at the Las Vegas laboratory. Certified values were available for the mercury and cadmium content of two samples (NBS Standard Reference Materials for coal and orchard leaves) but not for the other three samples (soil and fish and plant tissue). Satisfactory confirmation was obtained for mercury data, but INAA was not sensitive enough to detect cadmium in four of the five samples (Table 3).

Later, the ACB was asked to determine concentrations of 20 specific elements in 30 plant tissue samples and 3 soil samples. These samples were collected at three sites at varying distances downwind from a power plant in the Four Corners area of the western United States. Concentration data were needed for six elements (Be, Pb, Ni, Se, F, and S) that could not be determined satisfactorily by INAA, because detection limits for these elements are higher than the concentrations expected in these samples. Since these elements can be detected with SSMS at a lower level ($\sim$1 ng/g) than with INAA ($\leq$1 μg/g), SSMS was expected to be the more useful analytical technique.

All 33 samples were analyzed by SSMS; 3 soil samples and 20 plant samples were also analyzed by INAA. Samples of soil and three varieties of vegetation were collected at all three sampling sites, one of which was a control site. Five plant varieties were collected at only 2 sites; the remaining 11 plant varieties were collected at only one site.

Table 3. NEUTRON ACTIVATION DATA FOR MERCURY AND CADMIUM IN STANDARD SAMPLES

Sample	Mercury Concentration, μg/kg		Cadmium Concentration, μg/kg	
	INAA Data	Certified Value	INAA Data	Certified Value
NBS Orchard Leaves	151 [b]	155	N.D.	110
NBS Coal	120 [a]	130	N.D.	--
Oregano	654 [a]	--	N.D.	--
Tuna	366 [a]	--	N.D.	--
Mine Mtn. Soil #3	280 [a]	--	14,300	--

a Average of duplicate analyses

b Not detected; detection limit is ~1 μg/g

For SSMS analysis, weighed samples of approximately 10 g were ashed at 450°C for 4 hr. The residue was mixed and formed into an electrode. A single analysis by SSMS was performed on each sample, and no attempt was made to adjust sample size so that major elements could be determined quantitatively.

The INAA samples were irradiated in duplicate in plastic vials. Data were obtained after both long and short periods of irradiation. Long irradiation periods lasted 4 hours with subsequent counting for 600 sec after 4 days' decay; after 8 to 15 days these samples were counted again for 2 hours. Short irradiations lasted 3 to 30 sec; counting began as soon after irradiation as possible and lasted 600 sec. For elements measured after both long and short irradiations, separate isotopes were measured to provide independent confirmation; copper and potassium were exceptions. For these elements, the same isotopes were measured after both long and short irradiations.

Because many of the elements determined quantitatively by INAA exceeded the concentration range for SSMS, comparison of data from the two different techniques was frequently not possible. When possible, comparisons showed generally lower values were obtained by SSMS, especially for chlorine. The lower SSMS values for chlorine probably resulted from loss of organic chlorine during sample preparation.

Data interpretation by conventional analysis of variance showed that location of sampling site was insignificant as a source of experimental variance. However, factor analysis suggested 8 elements (I, Ba, Rb, La, Al, Mo, Ce, and Cl) may discriminate between samples taken at the control site and those taken at the other two sampling sites. Particular plant species are even more promising discriminators: Larrea divaricata with respect to I, Ba, and Cl content, and Ephedra nevadensis with respect to Al, La, Mg, and Zn content. Of these elements, only zinc is likely to be relatively more concentrated in fly ash than in the soil. Consequently, a large question remains as to whether the indicated correlation between location and the elemental content of these plants actually reflected contamination by the power plant plume.

The ACB's report to the EMSL concluded that these results did not provide conclusive evidence of soil and plant contamination from the power plant plume. However, these results may be helpful in planning similar future experiments. In such studies, samples of the suspected source of pollution should be taken to obtain plant tissue samples that are free of surface contamination by soil and that are as homogeneous as possible.

CHEMICAL ELEMENTS IN VARIOUS ENVIRONMENTAL SAMPLES

During the year, the ACB analyzed a variety of samples for the EPA's Region IV Surveillance and Analysis Division to assist them in locating pollutant sources. Their monitoring activities required multielement analyses of industrial wastewaters, reservoir water, river sediment, air particulates, and sewage sludge.

Survey analyses of the industrial wastewaters were requested to determine if pollutant discharge limits were exceeded. Multielement analysis by SSMS identified chemical elements present in significant concentrations and provided an elemental profile for each type of industrial effluent.

Most industrial wastewaters conformed to the appropriate discharge limits. Industries monitored included three can manufacturing plants, four steel mills, two synthetic fiber plants, a molecular sieve manufacturing facility, and a wire manufacturing plant. The wire plant wastewater contained excessive copper, lead, and zinc; the concentration of each element exceeded the total amount permitted for all heavy metals.

Other environmental samples were analyzed to help locate sources of specific pollution problems. Sediment from a stream used for cattle drinking water was analyzed to determine if heavy metal contamination could be causing cattle poisoning; no heavy metals were detected in significant concentrations. A fluffy air pollutant, which was collected by a citizen from his patio, was suspected to be insulation material emitted from a nearby insulation manufacturing plant. Data from SSMS analysis were compatible with the composition of the suspected material, perlite. Each of six sewage sludge samples contained 35-37 elements at concentrations ≥1 µg/l. A 5-day composite sample of reservoir intake water contained 25 elements at concentrations ≥1 µg/l.

Results of these analyses were reported to Region IV personnel for use in enforcement proceedings, when appropriate.

ORGANIC CONTAMINANTS IN NEW ORLEANS DRINKING WATER

In response to a request by the EPA's Region VI Surveillance and Analysis Division, the ACB identified and measured non-purgeable volatile organic compounds in a city drinking water. Because of allegations that the New Orleans, Louisiana, drinking water contained pollutants hazardous to consumers' health, state and city officials requested the EPA to examine the city's drinking water. This task required the cooperative efforts of several EPA laboratories. The ACB had demonstrated the use of combined gas chromatography-mass spectrometry for identification of specific organic contaminants in water [1-4] and had experience in sample extraction and separation techniques. Therefore, ACB personnel were asked to perform some analyses and to recommend extraction and separation procedures to be used.

The types and numbers of samples to be collected and analyzed were determined by EPA personnel in Region VI. Samples were collected by personnel from the EPA's Lower Mississippi River Facility (LMRF) at, Slidell, Louisiana, the Region VI laboratory that was responsible for coordination of this project.

ACB personnel analyzed various extracts from ten samples and their corresponding blanks. Gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC-MS) were used to identify and quantify as many as possible of the volatile organic components.

Sample Collection and Extraction

In July and August 1974, four types of samples were collected from three different water treatment plants serving the New Orleans metropolitan area. Region VI personnel collected three types of samples using carbon sorption techniques and extracted them with chloroform to remove sorbed organic material. At one water treatment plant, a large ("mega") sample was collected during a 7-day period by passing 1.1 million liters of water through approximately 20 kg of activated carbon. Carbon from this mega sampler was extracted at the EPA's Robert Taft Center in Cincinnati, Ohio. The carbon was extracted for 40 hr with approximate y 190 ℓ of chloroform in a large-scale reflux extraction unit. Excess chloroform was distilled off until about 2 liters remained in the pot.

A sample from each of the three water treatment plants was collected by passing 25,500 ℓ of water through two Pyrex cy inders, each containing approximately 340 g of activated charcoal, connected in series. This sample, which was collected over a 7 day period, represented the theoretical amount a person would drink during 70 years at the rate of 1 ℓ/day. The carbon from each cylinder was extracted at the EPA's Robert S. Kerr Laboratory at Ada, Oklahoma, in a special room designed to minimize contamination. Chloroform extraction for 48 hr in a Soxhlet apparatus was followed by vacuum concentration of the extract at temperatures ≤27°C to a volume of 30 to 60 ml. After chloroform extraction, the first of the two carbon filters in series was also extracted with ethyl alcohol.

At each of the three sites, the third type of carbon adsorption sample was collected during a two-day period by passing 60 ℓ of water through a small polyvinyl chloride tube containing approximately 70 g of carbon. Each of these samples was assumed to be equivalent to a person's water consumption during 2 months. These samples were extracted at the EPA's Region VI laboratory in Houston, Texas. A final volume of 25 ml was obtained after extraction in a Soxhlet apparatus.

ACB personnel participated in collection of the other two types of samples, which were concentrated using resin adsorption and tetralin extraction techniques. The resin adsorption technique had been developed[7] by Gregor Junk (Ames Laboratory, Iowa State University, Ames, Iowa) who participated in this project. Small glass columns containing cleaned Rohm and Haas XAD-2 resin were connected to finished water lines at all three treatment plants, and approximately 320 ℓ of water were passed through each tube. Ethyl ether extracts of these samples were concentrated to 1 ml.

A high-boiling solvent, tetralin (1,2,3,4-tetrahydronaphthalene), was used to extract triplicate samples from all three water treatment plants. This technique, originally suggested by B. F. Dudenbostel of EPA's Region II, permits GC analysis of the very volatile components that elute with and are obscured by conventional solvents, such as chloroform. A 2-ml portion of tetralin was used to extract each of three 1-ℓ water samples from each plant.

Each sample extract or blank extract was placed in an appropriate container and shipped to the ERLA for analysis by GC and GC-MS. Portions of the resin extracts were also analyzed by GC and GC-MS at the Ames Laboratory.

Extract Concentration and Separation Procedures

Mega Sample--

At the ERLA the chloroform extract of the mega sample was concentrated in a Kuderna-Danish apparatus to make 1 ml of each extract equivalent to 1 ℓ of water passed through the filter. Several fractionation techniques were investigated to obtain the best feasible GC separation of sample components. Solubility separation of the total extract into acid, basic, and neutral fractions showed that most sample components were neutral compounds, but did not improve GC separation significantly. Steam distillation neatly separated the extract into volatile distillable and non-distillable components but did little to improve GC separation of chromatographable components. No polynuclear aromatic hydrocarbons were detected by thin layer chromatography using techniques designed to isolate this class of compounds. However, two chlorinated pesticides were detected by electron capture GC after fractionation by column chromatography.

Seventy-year Samples--

Extracts of the 70-year sample filters, which had sorbed organic material from 25,500 ℓ of water were also concentrated to make 1 µl equivalent to 1 ℓ of filtered water. As with the mega sample, column chromatography was used to fractionate the chloroform extracts of the 70-year sample filters from one water treatment plant.

Two-month Samples--

Chloroform extracts of the 2-month samples were concentrated in a Kuderna-Danish apparatus to 0.3 µl to make 1 µl of extract equivalent to 100 ml of filtered water.

Resin Samples--

Ethyl ether extracts of the XAD-2 resin filters were concentrated to 1 ml in a micro Kuderna-Danish apparatus. Further solvent evaporation with a stream of dry nitrogen reduced the volume to make 1 µl equivalent to 1 ℓ of filtered water.

Tetralin Extracts--

Because the tetralin extracts were obtained to identify very volatile water contaminants, these extracts could not be concentrated by solvent evaporation.

Analysis

All sample extracts and blanks were analyzed by gas chromatography (flame ionization detector). After preliminary examination by GC techniques, low resolution electron impact mass spectral data were acquired with a computer-controlled GC-MS system. Some samples were also analyzed with electron capture GC and with chemical ionization and high resolution electron impact GC-MS systems.

Preliminary identifications of sample components were obtained by computer matching of unknown mass spectra with standard mass spectra in a central data bank and by visual comparison of unknown spectra to standard spectra in scientific publications or on file at the ERLA. When possible, standard samples were obtained to confirm tentative identifications by comparing GC retention time data and mass spectra of sample components with those of standards analyzed under the same conditions. To confirm the presence of two sample components, combined gas chromatography-Fourier transform infrared spectrophotometry was used to compare data from sample components and reference compounds.

Quantitative data were calculated from GC peak area measurements. Atrazine, a compound present in all the New Orleans water extracts was chosen as an internal standard. Solutions of known amounts of pure reference compounds were prepared and mixed with a stock solution of the internal standard. The flame response and retention time of each reference compound relative to the internal standard were used to calculate sample component concentrations. In some cases, the flame response calculated for a reference compound was also used for other compounds of the same chemical class. Blank samples, which contained no atrazine, were spiked with this internal standard for component concentration calculations.

Results

Analysis by GC and GC-MS permitted tentative identification of 76 organic components of the drinking water extracts (Table 4); the presence of 49 of these compounds was confirmed. Of the 76 compounds, 9 were not specifically identified as to particular isomer, and 8 others were identified only by compound class or by certain structural features. Compounds present in blanks were not reported as sample components except in cases where at least five times greater amounts were found in the sample extract.

Calculated contaminant concentrations ranged from about 0.01 µg/l (the detection limit for most compounds identified by the techniques used) to 12 µg/l. Most compounds detected were present at the lower end of this range; the relationship between concentration level and the number of detected compounds is shown for two samples from one water treatment plant (Table 5). These calculated concentrations are only estimates; unknown carbon sorption/desorption characteristics of sample components preclude stating concentrations with a high degree of accuracy.

Table 5. CONCENTRATION CLASSIFICATION OF ORGANIC COMPOUNDS DETECTED IN NEW ORLEANS DRINKING WATER

Concentration Range, µg/l	Number of Compounds Detected	
	70-year Sample Extract	Mega Sample Extract
0.01-0.09	74	84
0.10-0.99	19	17
1.0 -10	4	2
Total	97	103

Fifteen compounds present in low concentrations (0.1 to 0.3 µg/l) produced usable mass spectra but were not identified. Many other compounds in even lower concentrations were detected by GC, but did not produce usable mass spectra. For example, about 100 peaks were counted in the gas chromatogram (from a packed column) of the chloroform extract of one 70-year sample, but only 47 compounds were identified.

Table 4. ORGANIC COMPOUNDS IDENTIFIED IN NEW ORLEANS DRINKING WATER

Compound Name	RRT[b]	Concentration, µg/l[a]									
		Water Treatment Plant A				Water Treatment Plant B			Water Treatment Plant C		
		Mega Sample CCE[c]	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract
Aliphatic Hydrocarbons											
1. n-decane[d]	0.48	0.06	--	2.4	--	--	2.0	--	--	2.0	--
2. decane, branched	0.44	0.03	0.02	5.8	--	--	5.4	--	--	5.2	--
3. n-dodecane[d]	0.67	--	0.01	0.10	--	--	0.40	--	--	0.37	--
4. n-nonane[d]	0.38	--	0.03	2.4	--	--	2.4	--	--	2.1	--
5. n-pentadecane[d]	0.86	--	0.03	--	--	--	0.10	0.01	--	0.10	<0.01
6. n-tetradecane[d]	0.80	--	0.02	0.10	--	--	0.10	--	--	0.12	--
7. n-tridecane[d]	0.72	--	0.01	0.30	--	--	0.17	--	--	0.20	--
8. n-undecane[d]	0.58	0.03	--	2.5	--	--	<10	--	--	2.1	--
9. undecane, branched	0.52	0.04	0.06	5.3	--	--	--	--	--	--	--
Halogenated Aliphatics											
10. bromodichloromethane	0.18	--	D[e]	--	<0.1	--	--	<0.1	--	--	--
11. bromoform[d,f]	0.32	--	0.57	--	--	--	--	--	--	--	--
12. chloroform[d]	--	--	--	--	--	--	--	--	--	--	--
13. dibromochloromethane[d]	0.23	0.6	1.1	<10	<0.1	0.4	--	<0.1	0.06	D[e]	--
14. dibromodichloroethane isomer	0.35	0.16	0.33	--	--	--	--	--	0.63	--	--
15. dichloroiodomethane	0.26	0.84	1.1	--	--	1.3	--	--	1.6	--	--
16. hexachloro-1,3-butadiene[d]	0.65	0.07	0.16	0.70	0.04	0.27		0.12	0.21		<0.01
17. hexachloroethane[d]	0.53	0.39	4.3	--	0.03	0.19	--	<0.1	0.30	--	--
18. pentachloroethane[d]	0.38	--	--	--	<0.1	--	--	--	--	--	--
19. 1,1,1,2-tetrachloroethane[d]	0.30	0.11	0.04	--	--	--	--	--	--	--	--
20. tetrachloroethylene[d]	0.26	--	--	<1	<0.1	0.20	<5	<0.1	0.20	<5	--
21. 1,1,2-trichloroethane[d]	0.21	<0.2	0.35	6.2	<0.1	0.45	8.5	<0.1	0.41	6.4	--

Table 4. ORGANIC COMPOUNDS IDENTIFIED IN NEW ORLEANS DRINKING WATER (Continued).

Compound Name	RRT[b]	Concentration, µg/l[a]									
		Water Treatment Plant A				Water Treatment Plant B			Water Treatment Plant C		
		Mega Sample CCE[c]	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract
22. 1,1,1-trichloropropane	~0.07	--	--	--	<0.1	--	--	--	--	--	--
23. 1,2,3-trichloropropane	0.36	<0.2	--	--		--	--	--	--	--	--
24. chlorinated, fluorinated hydrocarbon	0.78	--	<0.01	--	<0.1	--	--	<0.1	--	--	<0.1
25. chlorinated, fluorinated hydrocarbon	0.82	--	<0.01	--	<0.1	--	--	<0.1	--	--	<0.1
26. dichlorinated hydrocarbon, MW 200	0.82	0.05	--	--	--	--	--	--	--	--	--
27. dichlorinated hydrocarbon, MW 249	~1.0	<0.02	<0.04	--	--	D[e]	--	--	D[e]	--	--
Chlorinated Aliphatic Ethers											
28. bis(2-chloroethyl) ether[d]	0.44	--	0.04	--	--	0.16	--	--	0.12	--	--
29. bis(2-chloroisopropyl) ether[d]	0.51	D[e]	0.18	--	--	0.08	--	--	0.03	--	--
Aromatic Hydrocarbons											
30. C_2-alkylbenzene	0.35	0.05	0.03	7.5	--	--	5.6	--	--	6.2	--
31. C_3-alkylbenzene	0.42	0.01	--	2.4	--	--	1.9	--	0.03	2.2	--
32. C_4-alkylbenzene	~0.52	--	<0.1	--	--	--	--	--	--	--	--
33. ethylbenzene	0.32	0.02	--	2.3	--	--	1.6	--	--	1.8	--
34. m-ethyltoluene[d]	0.42	--	--	--	--	0.05	--	--	0.02	--	--
35. o-ethyltoluene[d]	0.45	--	--	--	--	0.04	--	--	0.02	--	--
36. toluene[d]	0.22	0.08	--	11	--	0.16	7.1	<0.01	--	12	--
37. trimethylbenzene isomer	0.46	0.02	0.04	6.1	0.01	--	5.1	--	0.02	5.3	--
38. o-xylene[d]	0.33	0.12	0.33	4.1	--	--	2.8	--	--	3.4	--

Table 4. ORGANIC COMPOUNDS IDENTIFIED IN NEW ORLEANS DRINKING WATER (Continued).

Compound Name	RRT[b]	Concentration, µg/l[a]									
		Water Treatment Plant A				Water Treatment Plant B			Water Treatment Plant C		
		Mega Sample CCE[c]	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract	70-Year Sample CCE[c]	2-Month Sample CCE[c]	Resin Extract
Chlorinated Aromatics											
39. m-dichlorobenzene[d]	0.46	--	--	<3	--	--	--	<0.1	--	--	--
40. 1,2,3,4,5,7,7-heptachloronorbornene	0.94	0.03	0.06	--	0.02	0.07	--	0.04	0.07	--	0.01
41. heptachloronorbornene isomer	0.98	0.02	0.06	--	--	0.04	--	--	0.04	--	--
42. pentachlorophenyl methyl ether	[q]	<0.1	--	--	--	--	--	--	--	--	--
Herbicides and Related Compounds											
43. alachlor (Lasso)[d]	1.09	0.44	0.82	1.9	0.67	2.3	2.9	0.35	2.1	1.4	0.17
44. alachlor homolog (alachlor + 1 chlorine)	1.14	0.18	0.28	1.7	0.21	--	D[e]	--	0.05	D[e]	--
45. atrazine[d]	1.00	2.7	4.9[h]	3.7	1.0	5.2	4.8	0.64	5.4	3.2	0.16
46. atrazine homolog (atrazine - C_2H_4)	0.96	0.22	0.51	0.78	--	0.27	0.80	--	0.27	0.75	--
47. butachlor (Machete)[d]	1.21	0.02	0.05	--	<0.1	0.06	--	--	0.05	--	--
48. cyanazine (Bladex)[d]	1.13	<0.01	0.35	--	--	0.21	--	--	0.31	--	--
49. propazine[d]	~1.0	--	--	--	<0.1	0.1	--	--	<0.1	--	--
50. simazine[d]	~1.0	--	<0.1	--	--	<0.1	--	--	<0.1	--	--
Pesticides											
51. α-chlordane	[g]	<0.1	--	--	--	--	--	--	--	--	--
52. chlordene[d]	[g]	<0.1	--	--	--	--	--	--	--	--	--
53. dieldrin[d]	1.23	0.01	0.04	--	0.01	0.07	--	0.01	0.05	--	--
54. endrin[d]	1.27	0.004	--	--	--	0.008	--	--	0.006	--	--

Table 4. ORGANIC COMPOUNDS IDENTIFIED IN NEW ORLEANS DRINKING WATER (Continued).

Compound Name	RRT[b]	Concentration, µg/l[a] Water Treatment Plant A: Mega Sample CCE[c]	Water Treatment Plant A: 70-Year Sample CCE[c]	Water Treatment Plant A: 2-Month Sample CCE[c]	Water Treatment Plant A: Resin Extract	Water Treatment Plant B: 70-Year Sample CCE[c]	Water Treatment Plant B: 2-Month Sample CCE[c]	Water Treatment Plant B: Resin Extract	Water Treatment Plant C: 70-Hear Sample CCE[c]	Water Treatment Plant C: 2-Month Sample CCE[c]	Water Treatment Plant C: Resin Extract
Phthalates											
55. benzyl butyl phthalate[d]	1.29	0.24	0.64	1.4	--	0.83	1.8	--	0.75	1.6	0.08
56. dibutyl phthalate[d]	1.12	0.09	0.10	--	0.05	0.36	--	0.01	0.23	--	0.03
57. diethyl phthalate[d]	0.91	0.02	0.03	0.24	--	0.03	0.10	0.03	0.01	0.18	--
58. di-2-ethylhexyl phthalate[d]	1.38	11	0.10	0.40	0.05	0.46	0.50	--	0.27	1.2	0.16
59. dihexyl phthalate	1.24	--	0.03	--	0.05	--	--	--	--	--	0.16
60. diisobutyl phthalate[d]	1.06	0.59	--	<1	<0.05	--	--	--	--	--	--
61. dimethyl phthalate[d]	0.83	D[e]	0.27	0.60	--	0.13	0.82	--	0.18	0.74	--
62. dipropyl phthalate[d]	1.02	0.01	0.07	--	--	0.13	--	--	0.14	--	--
63. unknown phthalate	1.22	0.01	--	--	--	--	--	--	--	--	--
64. unknown phthalate	1.24	0.01	--	--	--	--	--	--	--	--	--
65. unknown phthalate	1.36	0.12	--	--	--	--	--	--	--	--	--
Miscellaneous											
66. benzaldehyde[d]	0.44	0.03	--	--	--	--	--	--	--	--	--
67. 2,6-di-t-butyl-p-benzoquinone[d]	0.84	--	0.22	--	--	0.21	--	--	0.25	--	--
68. di-2-ethylhexyl adipate[d]	1.32	0.10	--	--	--	--	--	--	--	--	--
69. dihydrocarvone	0.63	--	0.14	--	--	0.06	--	--	0.07	--	--
70. ethyl acetate	--	--	--	--	D[e]	--	--	--	--	--	D[e]
71. isophorone[d]	0.60	--	--	--	--	--	--	--	--	--	--
72. limonene[d]	0.50	--	0.03	--	--	--	--	--	--	--	--
73. methyl benzoate[d]	0.58	--	--	--	--	--	--	<0.01	--	--	--
74. 1,3,5-trimethyl isocyanurate[d]	0.73	0.01	0.01	--	--	--	--	--	--	--	--
75. triphenylphosphate[d]	1.31	0.03	0.12	--	--	--	--	--	--	--	--
76. unknown compound MW 145	~0.40	<0.3	<0.7	--	--	<0.9	--	--	<0.9	--	--

a Blank spaces indicate that the compound was not detected in that particular sample.

b GC retention time relative to the internal standard, atrazine.

c CCE = the chloroform extract of the carbon filter.

d The compound identification was confirmed by matching the mass spectrum and GC retention time of the sample component with those of a standard analyzed with the same instrumental conditions.

e Detected but not quantified because of low concentration or interference from other sample components.

f Chloroform was detected only in the tetralin extract of water from treatment plant A.

g Retention time not calculated; detected only in column chromatographic fraction.

h Includes the amount of atrazine found in the ethyl alcohol extract.

i The compound identification was confirmed by comparison of the infrared spectrum of the sample component with that of a standard; both spectra were obtained with a GC-FTIR system.

No carboxylic acids or phenols were identified in any of the sample extracts, including the carbon filter alcohol extract, which was examined before and after methylation with diazomethane. No polynuclear aromatic hydrocarbons were identified even after fractionation by thin layer chromatography. Some compounds (endrin, α-chlordane, chlordene, and pentachlorophenyl methyl ether) were not detected in the total extracts but were identified in fractions separated by column chromatography.

Identification of some compounds whose mass spectra were not in the central data bank or in spectra collections required special techniques. Other compounds were detected only after special sample treatment.

Dieldrin and Endrin--

These two organochlorine pesticides were detected by electron capture GC after fractionation of the mega-sample extract by column chromatography. The presence of both compounds was confirmed by matching retention times of sample components with those of standards using three different GC columns of varying polarity. Dieldrin was later detected in the total extract by GC-MS analysis but only by using a special technique. This pesticide was detected by computer searching for characteristic ions in the stored mass spectra collected with repetitive computer-controlled data acquisition as GC peaks eluted.

Simazine and Propazine--

Computer searching of stored spectra for characteristic ions also provided confirming evidence of the presence of simazine and propazine in water extracts. These two compounds were obscured in sample chromatograms by larger concentrations of atrazine, which had approximately the same retention time with the GC conditions used. Mass spectra acquired continually as the GC peaks eluted indicated that the atrazine peak was contaminated with other sample components; molecular ions and some significant fragments of these other components were observed. Computer searching for definitive ions indicated that simazine was present in the leading edge of the atrazine GC peak, and propazine was present in the trailing edge.

Alachlor--

The identification of a significant component of sample extracts from all three water treatment plants required a combination of analytical techniques. Its mass spectrum was not in the computerized data bank or in published spectra collections. The compound's molecular weight (269) was determined from its

chemical ionization mass spectrum. High resolution electron impact GC-MS data produced possible empirical formulae for the molecular ion and important fragment ions. Correlation of these data with reasonable fragmentation modes provided the most probable molecular formula. Alachlor, a herbicide with this molecular formula and the appropriate structural characteristics, was a reasonable contaminant. The sample component and a standard sample of alachlor produced the same low resolution mass spectra, had the same GC retention times, and produced matching infrared spectra (analysis by GC-FTIR). These data confirmed the identification of alachlor, 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide.

Alachlor Analog--

Some of the same techniques were used to identify a compound that produced a low resolution electron impact mass spectrum similar to that of alachlor. Chemical ionization and high resolution electron impact mass spectrometry provided additional structural information. These data indicated that the molecular structure of the sample component was very similar to that of alachlor. This unknown was identified as 2,2-dichloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, which is equivalent to alachlor with an additional chlorine. A standard was not available to confirm this tentative identification. Laboratory experiments indicated that this compound was not formed during chlorination treatment of water containing alachlor.

Trimethyl Isocyanurate--

By computer matching of mass spectra, one sample component was tentatively identified as trimethyl isocyanurate (1,3,5-trimethyl-2,4,6-trioxohexahydrotriazine). A reference sample of this compound was not commercially available but was synthesized at the Athens ERL. The identification was confirmed by matching the mass spectrum and GC retention time of the synthesized material with those of the sample component.

This study did not produce any conclusions as to the best sampling method. Analysis of only one sample type, whether the mega sample, the 70-year sample, the 2-month sample, or the resin sample, would not have permitted identification of all these 76 compounds. Although nine compounds were detected in the mega sample but not in the other three samples collected from Plant A, four of these nine compounds were detected in fractions obtained with column chromatography, which was not used for the other Plant A samples. More compounds were identified in the 70-year samples than in the 2-month or resin samples, but still more were identified when both 70-year and two-month samples were analyzed (Table 6).

Table 6. COMPARISON OF NUMBER OF IDENTIFIED COMPOUNDS IN DIFFERENT SAMPLE TYPES

Sample Type	Number of Identified Compounds
70-Year Samples	55
2-Month Samples	29
Resin Samples	28
70-Year and 2-Month Samples	60
70-Year and Resin Samples	53
2-Month and Resin Samples	42

The tetralin extracts proved to be too dilute for detection of any volatile components except chloroform, which was the only compound identified by this technique. Most GC peaks observed in tetralin sample chromatograms were also present in blank chromatograms. In the future, 1-ℓ samples will be extracted with 1 ml of tetralin that has been purified to eliminate interfering peaks. Whether this will increase the sensitivity of this technique enough to be useful for drinking water samples has not been determined.

In general, more compounds and higher concentrations were observed in carbon filter extracts than in resin extracts, but more data are needed to make valid comparisons of XAD resin and carbon filter sorption and extraction efficiencies.

The alcohol extract of the 70-year carbon filter produced only a few, poorly resolved GC peaks when examined without further treatment. Since most components were expected to be polar compounds such as carboxylic acids and phenols, the extract was methylated with diazomethane. Six compounds were identified in this methylated extract, but all were present and identified in the chloroform extract also. No carboxylic acids or phenols were found.

To obtain an indication of how well the organic contaminants were sorbed by the carbon filters, chloroform extracts of the two filters connected in series were analyzed separately for the 70-year sample. For each of the 29 compounds detected at a total concentration ≥0.04 μg/l, the percentage recovered in each filter was calculated (Table 7). Comparison of the amounts found on filters #1 and #2 showed that ≥96% of 24 compounds was extracted from filter #1. A general high degree of sorption was

indicated by the wide variety of compound classes included in these 24 compounds, but significant exceptions were noted. For example, more hexachloroethane was extracted from filter #2 than from filter #1, and only 64 to 85% of three trihalogenated methanes or ethanes was adsorbed by filter #1.

Comparison of sample component concentrations showed that up to 10 times higher concentrations of the lower-boiling compounds were found in the 2-month sample extract than in the 70-year and mega sample extracts. However, concentrations of the less volatile components were approximately the same in the three types of carbon extracts. Because the samples were not collected at the same time, contaminant concentrations could have changed, but concentration variations should not have been a function of volatility. These results suggest that the 70-year filter was overloaded with organic material, but this explanation is contradicted by recovery data (Table 7).

Concentrations of mega sample components were low compared to those of the 70-year sample. Of 30 compounds quantitated by both methods, 21 were found in the mega sample at concentrations only 25 to 76% of concentrations in the 70-year sample. Differences in solvent evaporation techniques may be partially responsible for the concentration discrepancies.

Results of these analyses of carbon and resin extracts were reported to the EPA's Region VI Surveillance and Analysis Division. The Athens ERL data were compiled with data from other laboratories participating in the survey of New Orleans drinking water contaminants and were incorporated into an EPA summary report[8]. These contaminant identifications and other data from the survey will permit other researchers to begin assessing the relationship between contaminants and public health.

ORGANIC CONTAMINANTS IN DRINKING WATER FROM 10 UNITED STATES CITIES

As part of a nationwide EPA survey of water supply systems, the ACB analyzed drinking water samples from 10 United States cities to identify organic components that were sorbed from water by carbon and desorbed from carbon by solvent extraction. This survey was initiated by the EPA Administrator, Russell E. Train, to identify and estimate the concentration of organic compounds in drinking water from all over the nation. Part of the survey required analysis of drinking water from 80 U.S. cities to determine concentrations of 6 specific halogenated compounds before and after disinfection by chlorination. These data were

Table 7. COMPARISON OF RECOVERIES FROM FILTERS #1 AND #2 OF THE 70-YEAR SAMPLE[a]

Compound	Total Concentration µg/l	% From Filter #1	% From Filter #2
Alachlor	0.82	97	3
Alachlor homolog	0.28	100	0
Atrazine	4.9	98	2
Atrazine, deethyl	0.51	96	4
Benzyl butyl phthalate	0.64	100	0
Bromoform	0.57	100	0
Butachlor	0.05	100	0
Cyanazine	0.35	100	0
Chlorodibromomethane	1.1	64	36
bis-2-Chloroethyl ether	0.04	100	0
bis-2-Chloroisopropyl ether	0.18	100	0
Dibromodichloroethane isomer	0.33	100	0
Dibutyl phthalate	0.10	80	20
2,6-Di-t-butyl-p-benzoquinone	0.22	100	0
Dichloroiodomethane	1.1	85	15
Dieldrin	0.04	100	0
Di-2-ethylhexyl phthalate	0.10	100	0
Dimethyl phthalate	0.27	100	0
Dipropyl phthalate	0.07	100	0
1,2,3,4,5,7,7-Heptachloronorbornene	0.06	100	0
Heptachloronorbornene isomer	0.06	100	0
Hexachloro-1,3-butadiene	0.16	100	0
Hexachloroethane	4.3	36	64
Isophorone	1.6	98	2
1,1,2-Trichloroethane	0.35	69	31
Trimethylbenzene isomer	0.04	100	0
Triphenyl phosphate	0.12	100	0
Undecane, branched	0.06	100	0
o-Xylene	0.33	100	0

[a]Only compounds present in total concentration of 0.04 µg/l or greater are included.

needed to determine the extent to which chlorination of drinking water forms new chlorinated compounds or increases the concentration of those already present. The six halogenated compounds sought were chloroform, bromodichloromethane, dibromochloromethane, bromoform, carbon tetrachloride, and 1,2-dichloroethane, several of which are so volatile that they require special analytical techniques.

Although more extensive analysis of the drinking water from all 80 cities was desirable, the more feasible approach was determined to be extensive analysis of drinking water from several cities that are scattered throughout the country and use water from several different types of sources. Therefore, 10 of the 80 cities were selected for further analysis. In an attempt to determine if certain types of source water contain fewer organic contaminants than other types, the 10 cities were selected to include 2 cities using water from each of 5 different source types, as follows:

Type of Source Water	Sample Site
Uncontaminated upland water	Seattle, Washington New York, New York
Ground water	Miami, Florida Tucson, Arizona
Water Possibly Contaminated by Agricultural Runoff	Otumwa, Iowa Grant Forks, North Dakota
Water Possibly Contaminated by Industrial Wastes	Cincinnati, Ohio Lawrence, Massachusetts
Water Possibly Contaminated by Municipal Wastes	Philadelphia, Pennsylvania Terrebonne Parish, Louisiana

The survey was coordinated by the EPA's Municipal Environmental Research Laboratory (formerly the Water Supply Research Laboratory) in Cincinnati, Ohio. They also analyzed samples from all 80 cities to determine concentrations of the 6 halogenated hydrocarbons and collected samples from 10 cities for analyses by the ACB.

At each sampling site, drinking water was passed through carbon filters for 7 days. Two cylindrical filters (3 in. x 18 in.), each containing approximately 340 g of granular activated carbon, were used to sorb organic contaminants from 6000 ℓ of

finished drinking water. To obtain reasonable blank samples, two filters that were to be used as blanks were placed behind two filters that had been flushed with 20 ℓ of water; 20 ℓ of drinking water were passed through all four filters connected in series. These samples were shipped to the EPA's Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma, where they were extracted with chloroform. The extracts were shipped to the Athens ERL for analysis by GC and GC-MS.

During January and February of 1975, samples were collected from the first five cities. Analysis of the chloroform extracts of these samples began in February. Comparison of gas chromatograms of sample extracts with those of corresponding blank extracts showed that the sample extracts were contaminated with organic compounds that apparently were on the carbon before samples were collected. Contamination of carbon used in the filters made these first samples useless. More than 11 times as much organic contamination was found in the carbon used to filter these water samples than was found in the carbon used for the New Orleans water samples. Since 26 times as much New Orleans water was passed through the same size filters, significantly less organic matter was adsorbed by filters used to collect samples from these five cities. After a cleaner carbon was located in sufficient amounts to complete sampling for the survey, water from the first five cities was resampled in March 1975. These chloroform extracts arrived at the Athens ERL in April 1975.

For analysis by GC and GC-MS, the chloroform extracts were concentrated to 6 ml, making 1 µl of sample extract equivalent to 1 ℓ of water passed through the carbon filter. Each blank was concentrated to a volume equivalent to its corresponding sample extract. A 30 m x 0.4 mm I.D. glass capillary GC column coated with SP-2100 was used to separate sample components. The improved separation available with this column had been demonstrated by comparison of chromatograms obtained with a packed GC column (SP2100 liquid phase; 10 ft x 1/8 in.) with those obtained with the capillary column. For example, 182 components were detected in a sample chromatogram from the capillary column, but only about half that many were detected when the same sample was analyzed with a packed column. The low flow rate for the capillary column carrier gas (approximately 2 ml/min) permitted direct coupling to the mass spectrometer without using an enrichment device. Since some sample is always lost through an enrichment device, its elimininationfrom the system increased the effective sensitivity of the analytical method. Because all GC eluants entered the mass spectrometer, the amount of injected sample was limited to 0.4 µl to avoid filament damage or excessive pressure in the ionizing region.

Sample components were identified and measured with the same GC and GC-MS techniques used for the New Orleans drinking water samples, except that concentration data were obtained from mass spectral data rather than GC data. With the computer-controlled system, mass spectra were acquired continuously as sample components eluted from the GC. After data acquisition, the spectra were retrieved from the storage device. Peaks similar to those in gas chromatograms were obtained by plotting total ion current versus spectrum number. Computer programs providing summations of ion current for each peak were used to calculate the approximate quantities of sample components after background data were subtracted. Calculations were based on data obtained from reference compounds analyzed under the same conditions as the sample. When a particular standard was not available, a reference compound of similar molecular structure was used to estimate the sample component concentration.

The reported concentrations (Table 8) are only approximations of amounts of organic compounds present in the water. Several factors affect analytical accuracy and precision: instrumental instability between analysis of the samples and reference compounds, variation of ionization between reference compounds and sample components of similar structure, and unknown carbon sorption/desorption characteristics of sample components. Because of these factors, a more precise calculation would not improve the accuracy of the reported concentrations.

Fifty different compounds were tentatively identified in the drinking water samples; 15 compounds were identified in more than one sample (Table 8). Thirty-four of these tentative identifications were confirmed by comparison of mass spectra and GC retention times of the sample component with those of a reference standard analyzed under the same conditions. Calculated concentrations of identified components varied from <0.01 to 30 µg/l. Of the 100 calculated concentrations, 55 were ≤0.09 µg/l and 34 were between 0.1 and 0.99 µg/l.

The data did not permit evaluation of the different types of source water; no valid conclusions could be reached as to the type containing fewer organic contaminants (Table 9). Some of the identified compounds may have resulted from chlorination, some may come from agricultural runoff, and some may occur naturally in water. However, most probably come from municipal or industrial waste discharges; many of the identified compounds were previously identified in industrial wastewaters[1-4,9-12]. No polynuclear aromatic hydrocarbons or polychlorinated biphenyls were among the identified compounds.

Analysis of the samples from the first five cities was completed in time for the data to be included in a report issued by the

Table 8. ORGANIC COMPOUNDS IDENTIFIED IN DRINKING OF 10 U. S. CITIES

Compound Name	Compound Concentration, µg/l[a]									
	Uncontaminated Upland Water Source		Ground Water Source		Source Contaminated by Agricultural Runoff		Source Contaminated by Industrial Wastes		Source Contaminated by Municipal Waste	
	Seattle	New York	Miami	Tucson	Ottumwa	Grand Forks	Cincinnati	Lawrence	Philadelphia	Terreborne Parish
Aliphatic Hydrocarbons										
1. 2-methyl-5-ethylheptane	--	--	--	--	--	--	--	--	--	0.01
2. n-nonane	--	0.02	--	--	--	--	--	--	--	--
Halogenated Aliphatic Hydrocarbons										
3. bromodichloromethane[b]	0.1	1.3	4.5	--	--	0.6	1.0	0.6	1.0	2.0
4. bromoform[b]	--	--	1.5	3.0	--	--	--	--	--	--
5. chlorodibromomethane[b]	--	0.4	15	0.01	--	0.1	0.5	0.01	0..	1.0
6. hexachloro-1,3,-butadiene[b]	--	--	--	--	--	<0.01	--	--	--	--
7. hexachloroethane[b]	--	--	0.5	--	--	--	--	--	--	--
8. isoamylchloride	--	0.01	--	--	--	--	--	--	--	--
9. tetrachloroethylene[b]	--	0.05	0.1	<0.01	--	0.2	0.1	0.07	--	--
Aromatic and Cyclic Hydrocarbons										
10. t-butyltoluene	--	--	--	--	--	--	--	--	0.01	--
11. p-ethyltoluene	0.05	--	--	--	--	--	--	--	--	--
12. isopropylbenzene[b]	--	--	--	--	--	--	--	--	--	0.01
13. isopropylmethylbenzene (cymene) isomer	--	--	0.1	--	--	--	--	--	--	--
14. n-propylbenzene	--	--	0.05	--	--	--	0.01	--	--	--
15. n-propylcyclohexane	--	--	0.2	--	--	--	--	--	--	--
16. tetramethylbenzene isomer	--	--	0.2	--	--	--	--	--	--	--

Table 8. ORGANIC COMPOUNDS IDENTIFIED IN DRINKING OF 10 U. S. CITIES (Continued).

Compound Name	Compound Concentration, µg/l[a]									
	Uncontaminated Upland Water Source		Ground Water Source		Source Contaminated by Agricultural Runoff		Source Contaminated by Industrial Wastes		Source Contaminated by Municipal Waste	
	Seattle	New York	Miami	Tucson	Ottumwa	Grand Forks	Cincinnati	Lawrence	Philadelphia	Terreborne Parish
Chlorinated Aromatics										
17. chlorobenzene[b]	--	--	1.0	--	--	--	--	--	--	--
18. p-chlorotoluene[b]	--	--	1.5	--	--	--	--	--	--	--
19. o-dichlorobenzene[b]	--	--	1.0	--	--	--	--	--	--	--
20. m-dichlorobenzene[b]	--	--	0.5	--	--	--	--	--	--	--
21. p-dichlorobenzene[b]	--	--	0.5	--	--	--	--	--	--	--
Aldehydes										
22. acetaldehyde[b]	0.1	--	--	--	--	--	--	--	0.1	--
23. 2-ethylbutanal	--	0.05	--	--	--	0.02	--	0.04	--	0.01
24. 3-methyl-3-pentanal	--	--	--	--	1.0	--	--	--	--	--
25. n-pentanal	--	--	--	--	0.5	--	--	--	--	--
26. trichloroacetaldehyde (chloral)[b]	3.5	0.02	--	--	--	0.01	2.0	--	5.0	1.0
Ketones										
27. acetone[b]	1.0	--	--	--	--	--	--	--	--	--
28. acetophenone[b]	--	--	--	--	--	--	--	--	1.0	--
29. camphor[b]	0.5	--	0.5	--	0.1	--	0.1	--	--	--
30. cyclohexanone[b]	--	--	--	--	0.1	--	--	--	--	--
31. 2,6-di-t-butyl-p-benzoquinone[b]	--	--	0.1	--	--	--	--	--	--	--
32. di-t-butyl ketone	--	--	--	--	--	--	--	0.02	--	--
33. 2-methylhexa-3-ene-2-one	--	0.07	--	--	--	--	--	--	--	--
34. 2-pentanone[b]	--	--	--	--	0.1	--	--	--	--	--
35. 1,1,3,3-tetrachloro-2-propanone[b]	--	--	0.2	--	--	--	0.5	--	1.0	--

Table 8. ORGANIC COMPOUNDS IDENTIFIED IN DRINKING OF 10 U. S. CITIES (Continued).

Compound Name	Compound Concentration, µg/l[a]									
	Uncontaminated Upland Water Source		Ground Water Source		Source Contaminated by Agricultural Runoff		Source Contaminated by Industrial Wastes		Source Contaminated by Municipal Waste	
	Seattle	New York	Miami	Tucson	Ottumwa	Grand Forks	Cincinnati	Lawrence	Philadelphia	Terreborne Parish
Herbicides and Pesticides										
36. atrazine[b]	--	--	--	--	0.1	--	--	--	--	--
37. lindane (α-BHC)[b]	--	--	--	--	--	--	0.01	--	--	--
Phthalates										
38. di-n-butyl phthalate[b]	0.01	--	5.0	--	0.1	--	--	0.01	0.05	0.02
39. diethyl phthalate[b]	0.01	0.01	1.0	--	--	--	0.1	0.04	0.01	--
40. di-2-ethyhexyl phthalate[b]	--	--	30	--	--	--	--	0.08	0.5	0.04
41. di-n-propyl phthalate[b]	--	--	0.5	--	--	--	--	--	--	--
Miscellaneous Compounds										
42. diethyl malonate[b]	--	--	--	--	0.1	--	0.01	--	--	--
43. 1,4-dioxane[b]	--	--	--	--	--	--	--	0.01	--	--
44. methylethylmaleimide	--	0.02	--	--	--	--	--	--	--	--
45. β-santalene	0.01	--	--	--	--	--	--	--	--	--
46. α-terpineol[b]	--	--	--	--	0.5	--	--	--	--	--
47. tetramethyltetrahydro-furan isomer	--	--	--	--	--	--	--	--	--	--
48. tri-n-butylphosphate[b]	--	--	0.5	--	--	--	0.05	--	--	--
49. trichlorinitromethane (chloropicrin)[b]	--	--	--	--	0.05	--	--	--	--	--
50. trimethylisocyanurate	--	--	--	--	--	--	0.5	--	--	--

[a] Blank spaces indicate that the compound was not detected in that particular sample.

[b] The compound identification was confirmed by comparison of the mass spectrum and GC retention time of the sample component with those a standard analyzedwith the same instrumental conditions.

EPA in June 1975[13]. Data for all 10 samples were reported to the project coordinator at the EPA's Municipal Environmental Research Laboratory in Cincinnati, Ohio, where they were compiled with results of analyses performed by that laboratory. These data will be used in future research projects designed to determine the health significance of the compounds at the levels found in water, to investigate their sources, and to evaluate techniques for preventing their presence in water.

DISSEMINATION OF ANALYTICAL INFORMATION

The ACB's analytical expertise was utilized by universities, colleges, local schools, scientific organizations, industrial laboratories, a congressman, and state and federal agencies. In addition to the usual requests for publication reprints, standard samples, and information about analytical methods, the ACB responded to a variety of requests for assistance.

Consultations

- Assistance with identification of rat metabolites of Arochlor 1016, a commercial polychlorinated biphenyl mixture, was given to scientists from a university medical school.

- The use of capillary columns for improved GC separation of complex mixtures of organic compounds was demonstrated at a Cincinnati, Ohio, EPA laboratory, where an ACB-prepared capillary column was installed in a GC-MS system used for pollutant identifications.

- The EPA's laboratory at Gulf Breeze, Florida, requested assistance with an analytical method for nitrilotriacetic acid in seawater; the ACB provided advice and training in the operation of a differential pulse polarograph.

- Each of two university seniors, both chemistry majors, received 4 weeks of training in current methods of water pollution analysis. ACB personnel directed their work on identification of organic compounds in raw and treated paper mill wastewaters and in municipal wastewater before and after chlorination.

- Throughout the year, all EPA laboratories with computerized GC-MS systems were given assistance with the use of minicomputer programs for data

Table 9. CLASSIFICATION OF IDENTIFIED COMPOUNDS ACCORDING TO TYPE OF SOURCE WATER

Source Type	Number of Compounds Identified		
	City #1	City #2	Both Cities
Uncontaminated Upland Water	9	10	3
Ground Water	22	3	3
Contaminated by Agricultural Runoff	11	6	0
Contaminated by Industrial Wastes	12	9	4
Contaminated by Municipal Wastes	10	8	5

manipulation and with the mass spectra matching program that compares sample spectra obtained in individual laboratories with standard spectra stored in a central data bank[14].

- The mass spectra matching program was used at the Athens ERL by a scientist from the National Institute of Environmental Health Sciences, where the necessary computerized equipment was not available. Mass spectra obtained with a GC-MS system in the North Carolina laboratory were brought to the Athens ERL and were compared with standard spectra stored in the central data bank.

- A college professor who was working on the problem of prevention of accumulation of s-triazine herbicides in soils was provided a low resolution electron impact mass spectrum of a reaction product of atrazine.

- The use of a combined gas chromatography and Fourier transform infrared spectrophotometry (GC-FTIR) system, which is still in the developmental stage and is not readily available in analytical laboratories, was demonstrated to a pesticide manufacturer. The GC-FTIR system was used to analyze a complex mixture of metabolites isolated from food crops (corn and oranges) that had been treated with a newly developed pesticide.

- At the request of the EPA's office of Program Integration, the ACB participated in planning and preparing a thorough critical review of all available data that pertain to setting effluent guidelines and standards for mercury and its compounds in air, water, and solid wastes.

- Several reports and research proposals were reviewed by ACB personnel having expertise in the particular subjects being addressed. These included a manuscript on characterization of polychlorinated biphenyls in the marine environment, a comprehensive report on the environmental impact of asbestos and mercury, research proposals in response to the EPA's stated need for identification and quantification of organic compounds in surface waters from selected industrialized areas of the United States, a contractor's plans for electrochemical treatment of textile dye wastes, and a study of organic pollutants in industrial effluents and their fate in receiving waters. The latter project, which was sponsored by

the National Science Foundation, involved assistance in planning and reviewing the proposal, contacting prospective industries, planning sampling sites and schedules, and reviewing research results and reports.

- At the request of the local school system, ACB personnel made several educational presentations to acquaint students with water pollution projects at the Athens ERL.

- The office of a Maryland congressman concerned with water pollution was given a list of all the organic compounds that the ACB has identified three or more times in waters of all types.

Symposia

During FY 75, ACB personnel planned and arranged three scientific symposia. On May 19-21, 1975, the Fifth Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants was held at Jekyll Island, Georgia. It was sponsored by the U.S. Environmental Protection Agency, the University of Georgia, and the Division of Environmental Chemistry and Analytical Chemistry of the American Chemical Society. The symposium's purpose was to provide a forum for communication between environmental analytical chemists and experts in advanced analytical techniques with environmental applications. The 225 participants, including 27 from 9 foreign countries, represented diverse analytical interests and were about evenly distributed among industry or research institutes, academic institutions, and government facilities.

An ACB scientist organized a special symposium, The Identification and Analysis of Organic Pollutants in Water, which was held in conjunction with the First Chemical Congress of the North American Continent in Mexico City on November 31-December 5, 1975. This symposium was sponsored by the American Chemical Society as well as Canadian and Mexican chemical organizations. The 48 invited speakers presented results of recent research activities at various types of scientific organizations concerned with water pollution. This symposium promoted international cooperative efforts toward preventing and controlling water pollution on the North American continent.

A symposium on Trace Analysis was organized and conducted for the American Society for Mass Spectrometry. It was held during the twenty-third annual conference of the Society in Houston, Texas, during the week of May 26, 1975. Approximately 100 conference participants attended the 12 research presentations.

SECTION IV

REFERENCES

1. Keith, L. H. and S. H. Hercules. Environmental Applications of Advanced Instrumental Analyses: Assistance Projects, FY 69-71. U. S. Environmental Protection Agency, Athens, Georgia. Publication Number EPA-R2-73-155. May 1973. 83 p.

2. Alford, A. L. Environmental Applications of Advanced Instrumental Analyses: Assistance Projects, FY 72. U. S. Environmental Protection Agency, Athens, Georgia. Publication Number EPA-660/2-73-013. September 1973. 46 p.

3. Alford, A. L. Environmental Applications of Advanced Instrumental Analyses: Assistance Projects, FY 73. U. S. Environmental Protection Agency, Athens, Georgia. Publication Number EPA-660/2-74-078. August 1974. 31 p.

4. Alford, A. L. Environmental Applications of Advanced Instrumental Analyses: Assistance Projects, FY 74. U. S. Environmental Protection Agency, Athens, Georgia. Publication Number EPA-660/4-75-004. June 1975. 30 p.

5. McGuire, J. M., A. L. Alford, and M. H. Carter. Organic Pollutant Identification Utilizing Mass Spectrometry. U. S. Environmental Protection Agency, Athens, Georgia. Publication Number EPA-R2-73-234. July 1973. 48 p.

6. Webb, R. G., A. W. Garrison, L. H. Keith, and J. M. McGuire. Current Practices in GC-MS Analysis of Organics in Water. U. S. Environmental Protection Agency, Athens, Georgia. Publication Number EPA-R2-73-277. August 1973. p. 5-13.

7. Junk, G. A., J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arquillo, R. Vick, H. J. Svec, J. S. Fritz, and G. V. Calder. Use of Macroreticular Resins in the Analysis of Water for Trace Organic Contaminants. J. Chromatogr. 99, 745-762, 1974.

8. Region VI, Surveillance and Analysis Division. New Orleans Area Water Supply Study. U. S. Environmental Protection Agency. Publication Number 906/9-75-003. September 1975.

9. Keith, L. H. Chemical Characterization of Industrial Effluents. (Presented at the 163rd National Meeting of the American Chemical Society, Division of Water, Air, and Waste Chemistry, Boston, Massachusetts, April 1972.)

10. Keith, L. H. and J. M. McGuire. Computer-Controlled Mass Spectral characterization of Industrial Organic Pollutants. (Presented at the 164th National Meeting of the American Chemical Society, Division of Water, Air, and Waste Chemistry, New York, NY, August 1972.)

11. Keith, L. H. Chemical Characterization of Industrial Wastewaters by Gas Chromatography-Mass Spectrometry. Sci. Total Environ. 3, 87-102, 1974.

12. Keith, L. H. Analysis of Organic Compounds in Two Kraft Mill Wastewaters, U. S. Environmental Protection Agency, Athens, Georgia. Publication No. EPA-660/4-75-005. June 1975. 99 p.

13. Preliminary Assessment of Suspected Carcinogens in Drinking Water, Interim Report to Congress. U. S. Environmental Protection Agency, Washington, DC. June 1975. 33 p. Appendices I-VI, 214 p.

14. Heller, S. R., J. M. McGuire, and W. L. Budde. Trace Organics by GC/MS. Environ. Sci. Technol. 9, 210-213, 1975.